

gold nanoparticles (652 μl , 9.7 nM) and 2-modified gold nanoparticles (652 μl , 9.7 nM) were added to linker DNA 3, 4, or 5 (30 μl , 10 nM). After full precipitation, the aggregates were washed with 0.3 M $\text{CH}_3\text{COONH}_4$ solution to remove excess linker DNA and NaCl.

Lyophilization (10^{-3} ~ 10^{-2} torr) of the aggregate to dryness results in pellets and removal of the volatile salt, $\text{CH}_3\text{COONH}_4$. Unfunctionalized, citrate-stabilized particles, prepared by the Frens method, (Frens, *Nature Phys. Sci.* **241**:20-22 (1973)) were dried as a film and used for comparison purposes. The resulting dried aggregates had a color resembling tarnished brass and were very brittle. FE-SEM images demonstrated that oligonucleotide-modified nanoparticles remained intact upon drying, while citrate-stabilized nanoparticles fused to one another. Significantly, the dried DNA-linked aggregates could be redispersed in 0.3 M PBS buffer (1 ml), and exhibited excellent melting properties; heating such a dispersion to 60 $^{\circ}\text{C}$ resulted in dehybridization of the DNA interconnects, yielding a red solution of dispersed nanoparticles. This combined with the FE-SEM data conclusively demonstrated that DNA-modified gold nanoparticles are not irreversibly aggregated upon drying.

The electrical conductivities of the three samples (dried aggregates linked by 3, 4, and 5, respectively) were measured using a computer-controlled, four-probe technique. Electrical contacts consisted of fine gold wires (25 and 60 μm diameter) attached to pellets with gold paste. Samples were cooled in a moderate vacuum (10^{-3} to 10^{-2} torr), and conductivity was measured as the temperature was increased under a dry, low pressure of helium gas. The sample chamber was insulated from light in order to eliminate possible optoelectronic effects. Excitation currents were kept at or below 100 nA, and the voltage across the entire sample was limited to a maximum of 20 V. Surprisingly, the conductivities of the aggregates formed from all three linkers, ranged from 10^{-5} to 10^{-4} S/cm at room temperature, and they showed similar temperature dependent behavior. The conductivities of the DNA-linked aggregates showed Arrhenius behavior up to about 190 $^{\circ}\text{K}$, which is characteristic of a semiconducting material. This is similar to the behavior of activated electron hopping observed in discontinuous metal island films (Barwinski, *Thin Solid Films*

128:1-9 (1985)). Gold nanoparticle networks linked by alkanedithiols have shown similar temperature dependence (Brust et al., *Adv. Mater.* 7:795-797 (1995); Bethell et al., *J. Electroanal. Chem.* 409:137-143 (1996)). Activation energies of charge transport can be obtained from a plot of $\ln \sigma$ versus $1/T$ using equation (1).

$$\sigma = \sigma_0 \exp[-E_d/(kT)] \quad (1)$$

The average activation energies calculated from three measurements were 7.4 ± 0.2 meV, 7.5 ± 0.3 meV, and 7.6 ± 0.4 meV for the 24-, 48-, and 72-mer linkers, respectively. Conductivity data from 50°K to 150°K were used for these calculations.

Since the electrical properties of these types of materials should depend on the distance between particles, synchrotron SAXS experiments were used to determine interparticle distances of the dispersed and dried aggregates. The SAXS experiments were performed at the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT) Sector 5 of the Advanced Photon Source, Argonne National Laboratory. DNA-linked aggregates and dilute samples of DNA-modified colloid were irradiated with an 0.3 micron beam of 1.54 Å radiation, and scattered radiation was collected on a CCD detector. The 2D data were circularly averaged and transformed into a function, $I(s)$, of the scattering vector magnitude, $s = 2\sin(\theta)/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident radiation. All data were corrected for background scattering and sample absorption. The first peak position, which is sensitive to interparticle distance, drastically changed from s values of 0.063 nm^{-1} , 0.048 nm^{-1} , and 0.037 nm^{-1} for the 24-, 48-, and 72-mer linked aggregates, respectively, to an s value of 0.087 nm^{-1} upon drying for all three aggregates structures. This indicates that interparticle distances decreased significantly upon drying, to the point where the particles were almost touching, and that such distances were virtually independent of linker length, while those in solution were highly dependent on linker length. This explains why similar activation energies were observed for the three different linker systems in the dried pellet conductivity experiments. Moreover, it also explains why

relatively high conductivities were observed, regardless of how one views the electronic properties of DNA. Unlike the DNA-linked materials, the dried film of citrate-stabilized gold nanoparticles showed metallic behavior. This is consistent with the SEM data, which showed that such particles fuse together.

Above 190°K, the measured conductivities of the DNA-linked samples showed an anomalous dipping behavior. For all samples, the conductivity started to decrease abruptly at approximately 190°K and continued to decrease until approximately 250°K, at which point it increased again. To investigate this unusual behavior in detail, the electrical conductivity was measured as the sample was cooled and warmed repeatedly. Interestingly, the dip in conductivity only occurred in the direction of increasing temperature. Since DNA is hydrophilic and water could potentially affect the electrical properties of the hybrid structures, the effect of relative humidity on the conductivity of the gold aggregates was examined. The resistance increased by a factor of 10 with increasing humidity from 1% to 100%. It should be noted that the characteristic dip was very weak when the sample was kept in vacuum (10^{-6} Torr) for 48 hours prior to the conductivity measurement. From these observations, it was concluded that the unusual dip and subsequent rise in conductivity above 190°K is associated with water melting and the hygroscopic nature of the DNA, which temporarily increased the interparticle distance (until evaporation took place). Consistent with this hypothesis, SAXS measurements on a dried aggregate that was wetted with 0.3 M PBS buffer showed a 200% increase in interparticle distance (~2 nm).

These studies are important for the following reasons. First, they show that one can use the molecular recognition properties of DNA to assemble nanoparticle-based materials without passivating them or destroying their discrete structural or electrical properties. If these DNA-functionalized particles are to be used to study electrical transport in three-dimensional macroscopic assemblies or even lithographically patterned structures (Piner et al., *Science* 283:661-663 (1999)), it is imperative that their electrical transport properties be delineated. Second, it shows that over a fairly long linker distance (8 ~ 24 nm), the conductivities of the dried assemblies are virtually independent of DNA linker length. This